J. Environ. Nanotechnol.
Volume 5, No.3(2016) pp. 20-23
ISSN (Print): 2279-0748
ISSN (Online): 2319-5541
doi:10.13074/jent.2016.09.163204

A New Route for Nanocomposite Photocatalyst Mediated Synthesis of 2,5-dimethylpyrazine

V. Kandavelu[1,2 *], R. Renganathan[3]

[1]*Department of Chemistry, Sri Shakthi Insttitute of Engineering & Technology, Coimbatore, TN, India.*
[*2,3]*School of Chemistry, Bharathidasan University, Tiruchirappalli, TN, India.*

Received: 15.04.2016 Accepted:19.07.2016

Abstract

Synthesis of N-containing heterocyclic compound, 2,5-dimethylpyrazine,is reported with moderate yields. It is achieved by heterogeneous photocatalysis at room temperature from inexpensive and readily available reactants i.e., propylenediamine and propylene glycol by cyclization. Various semiconductor supported zeolite photocatalysts were used for the synthesis in the acetonitrile medium. The reaction conditions have been optimized to get the maximum yield by modifying the catalyst, mole ratio of the reactants and irradiation time. ZSM-5 with 5% TiO_2gives higher yields up to 32.4 mol %.

Keywords: *Dimethyl Pyrazine; Photocatalysis; Synthesis; Titanium dioxide; Zeolite.*

1. INTRODUCTION

The chemistry of heterocyclic compounds is one of the interesting branches in organic chemistry because of diversity of synthetic procedures, physiological and industrial significance. The synthesis of pyrazines and its derivatives has received growing interest due to their applications in pharmaceutical and perfumery industries. The importance of these molecules has provided the interest to develop environmentally friendly and more convenient procedures. Numerous reports have been published relating to synthesis (Su *et al.* 1988; Chang *et al.* 1989; Subbarao *et al.* 2003; Subbarao *et al.* 2002) and TiO_2 mediated organic reactions (Fox *et al.* 1983; Wang *et al.* 1997). The study of photochemistry of organic molecules adsorbed on TiO_2 loaded zeolite surfaces to conduct phototransformations have received greater attention as potential composite photocatalysts due to the unique pore size, shape selectivity and adsorption properties of zeolites, and the added photocatalytic property of TiO_2. 2,5-dimethylpyrazine is often used in food preparations. This compound is mainly used to confect the essence of cocoa, coffee, meat, or potato flavor and is also an ingredient in cigerettes. It is presently synthesized from 1-amino-2-propanol and is obtained as a mixture with its derivatives having low yields. The present study aimed to find a new photocatalytic route for the synthesis of 2,5-dimethylpyrazine (2,5-DMP) at room temperature.

**** V. Kandavelu Tel. No.: +91 99442 02965***
e-mail: vkands@gmail.com

2. MATERIALS & METHODS

2.1 Materials

The chemicals propylenediamine, propylene glycol, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, acetonitrile, ethanol, methanol, chloroform and silica gel were of high purity and used as such.

2.2 Preparation of Catalysts

The nanocomposite catalysts have been prepared by impregnation of TiO_2 on zeolites by thorough mixing of zeolites with a required amount of semiconductor such as TiO_2 corresponding to 2 and 5 wt % in agate motor with dry ethanol (Subba Rao *et al.* 2000). The ethanol was removed by evaporation and dried overnight in an air oven at 120 °C and then calcined at 400 °C for 6h. The prepared semiconductor (TiO_2) supported photocatalysts are HZSM-5 (Si/Al = 30), HY (Si/Al = 2.3) and Hβ (Si/Al = 20).

2.3 Photocatalytic Reaction Studies

The reactants propylenediamine and propylene glycol (2 mmol each) in acetonitrile (20 mL) were

stirred with 130 mg of catalyst and irradiated under the stream of molecular O_2 (20 mL/h) at room temperature using UV lamp ((3.0 mW cm-^{2}, 18 W x 5 Asram lamps, with a spectral range between 340 nm to 410 nm, where the maximum emission is at 365 nm)in a cylindrical quartz photoreactor for about 14 hours. The reaction mixture was centrifuged to separate the catalyst. The product was detected using methanol: chloroform (10:90) solvent system (by thin layer chromatography) and the product was separated by column chromatography using the same solvent system and was characterized by ^{1}H NMR, boiling point, MS, CHN analysis and GC-MS.

2.4 Analyses

The UV-Vis DRS measurements were performed on CARY 5 UV-Visible spectrometer with an integrating sphere reflectance accessory.The XRD patterns of all the catalysts in this study are obtained on a Siemens D5000 X-ray diffractometer using Ni filtered Cu Kα radiation (λ = 1.5406) from 2θ = 10 to 60°. TPD of ammonia experiments were conducted on an Autochem 2910 (Micromeritics, USA) instrument. A conventional all glass volumetric high vacuum system has been employed for the surface area measurements of the catalysts by nitrogen adsorption at liquid nitrogen temperature.Philips XL 30 SFEG instrument was employed for the Scanning Electron Microscope (SEM) measurement.The products were identified by a HPLC (Dionex) equipped with a UV-Vis detector (detector wavelength 260 nm) using LichrospherRP-18, $5\mu m$ column. An eluent containing acetonitrile: triethylammonium acetate buffer was used at a flow rate of one mL min^{-1} with a time gradient from t = 0 (A = 100 %, B = 0 %) to t = 25 min (A = 50 % and B = 50 %). Nuclear Magnetic Resonance (NMR) spectra was obtained on Bruker (200 mHz) spectrometer. Chemical shifts (δ) are given in ppm. Mass spectral measurements were recorded on ESI-MS (Electronspray Ionization Mass Spectroscopy) in acetonitrile. Elemental analysis (EA) were performed using Leco 900 (C,H,N detection) analyzers. The evolution of CO_2 from the irradiated samples was monitored by Gas chromatograph (HRGC 5300 Carlo Erba), equipped with a Porapak Q column (thermal conductivity detector) using helium as carrier gas.

3. RESULTS & DISCUSSION

3.1 Photocatalytic synthesis

The photocatalytic synthesis of 2,5-DMP by the cyclization of propylenediamine and propylene glycol was carried out over titanium dioxide (2 % & 5%) and supported over HY, Hβ and HZSM-5 zeolites. The present work has been initiated keeping in view that heterogeneous photocatalysis occurs on surface of titanium dioxide catalyst and adsorption can be modified due to incorporation of titania on the support and acidity of the zeolites. Here, we have carried out the intermolecular cyclization of propylenediamine and propylene glycol.

The progress of the reaction was monitored using HPLC technique by comparing it with authentic samples. The yields reported were estimated based on the HPLC peak area compared with authentic one. To get maximum yield, the reaction conditions were optimised by several trials and to compare the photocatalytic activity, parallel experiments were also carried out using bare TiO_2 and different semiconductor loaded zeolites. The results are summarized in table 1. The control experiments were performed to confirm whether the reaction is photocatalytic or non-photocatalytic. In the absence of oxygen, light or zeolite/TiO_2 and in the presence of zeolite alone, the reaction did not occur. It has been experimentally proved that the reaction is photocatalytic since this reaction proceeds only in the co-presence of oxygen, irradiation and a photocatalyst (zeolite/TiO_2). So it is concluded that light, semiconductor/zeolite and oxygen are required to produce 2,5-DMP, by the intermolecular cyclization of diaminoporpane and dihydroxypropane. In the semiconductor, light and O_2 (without zeolite) system, the reaction leads to the mineralization of reactants to CO_2. Also, either of the reactants in excess did not provide any better yields of 2,5-DMP. Bare semiconductor powder (TiO_2) photocatalyzed reaction did not also yield 2,5-DMP. The reaction, in this case, predominantly progressed to the total oxidation of reactants. Table 1 shows the results of the photocatlaytic cyclization of diaminopropane and dihydroxypropane in non-aqueous medium by various types of catalysts studied. No change in the physical properties of zeolite/TiO_2 was observed and XRD analysis confirms that no loss of crystallinity occurs after the modification and subsequent reaction. In this study, one of the best photocatalysts for the production of 2,5-DMP was found to be 5 wt% TiO_2/ZSM-5 with yield of 32.4 mol %. The channels in zeolites have to be sufficiently large to permit shape changes occurring during the reaction and to accommodate the formation of the required product. Differences observed in product yields between HY, Hβ and ZSM-5 support materials reveal that to obtain good product selectivity, an appropriate size of cavity has to be used. Zeolite ZSM-5 showed better yield when compared with Hβ and HY. The distribution of TiO_2 on zeolite Hβ and HY were not uniform, where as it is uniform in ZSM-5

(fig. 1). This may be the reason why ZSM-5 shows better yield. Also the present intermolecular cyclization reaction is favored by a combination of moderate hydrophobicity and acidity.

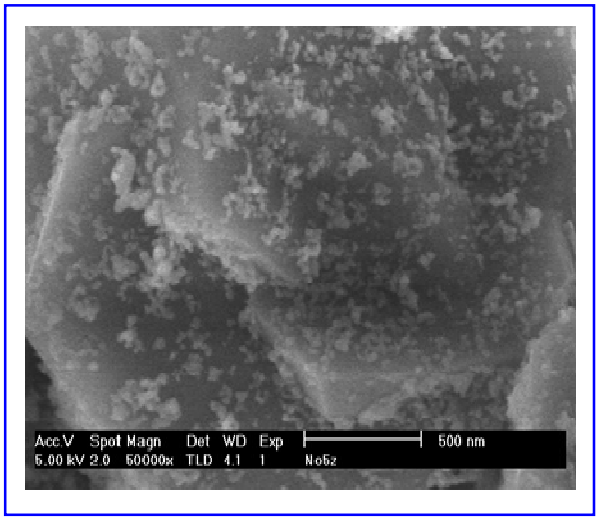


Fig. 1: SEM image of TiO_2 (5%) impregnated on ZSM5 zeolite

Table 1. Photocatalytic cyclization of diaminopropane and dihydroxy propane to 2,5-dimethylpyrazine achieved by semiconductor/ zeolite catalysts

Catalyst	SiO_2/ Al_2O_3 ratio	Surface area(m^2g^{-1})	Acidity (mmol g^{-1})	Isolated product (mol %)
2% TiO_2/Hβ	20	517	0.48	09.5
5% TiO_2/Hβ	20	470	0.42	18.0
2% TiO_2/HY	2.3	645	0.36	09.7
5% TiO_2/HY	2.3	624	0.30	22.8
2% TiO_2/ZSM5	30	348	0.29	07.5
5% TiO_2/ZSM5	30	320	0.23	32.4
50% TiO_2/ZSM5	30	220	0.18	36.6
TiO_2	-	50	-	-

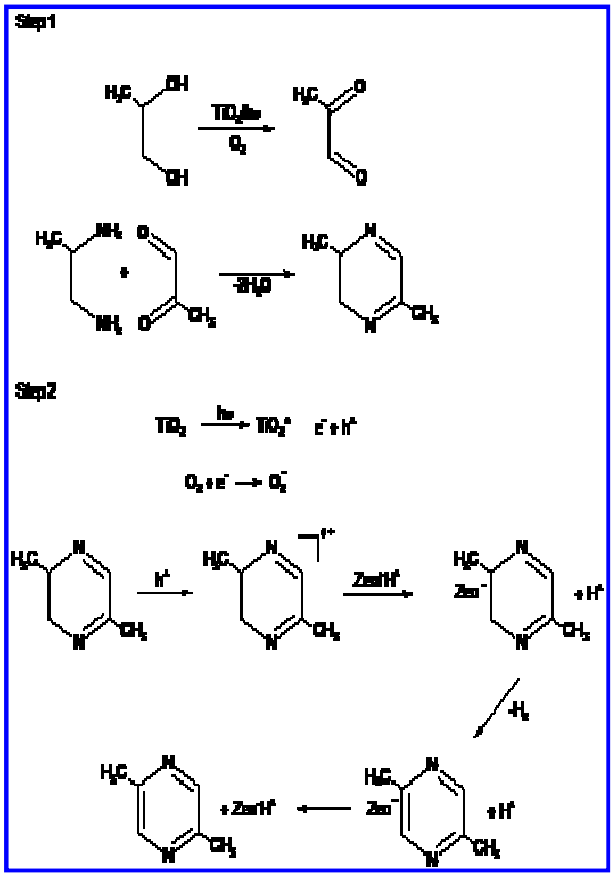
[a]Surface area measured with liquid N_2 at 77 K. TPD of NH_3 measured on Autochem 2910 (Micrometrics, USA). Irradiation 14h; 3 mW / cm^{-2} UV lamp, O_2 atmosphere).

The degree of total oxidation is strongly influenced by the % of TiO_2 loading in the zeolite. Higher loading (50% TiO_2) gives almost the same yield of 2,5-DMP when compared with 5% TiO_2 but alongwith some minor products. The minor products are probably due to the oxidation of 2,5-DMP (i.e., a methyl group oxidation to alcohol and further to aldehyde) which is confirmed by GC-MS. So the best nanocompositephotocatalyst for the production of 2,5-DMP alone is found to be 5 wt% TiO_2/ZSM-5. The catalyst showed consistent activity for at least 4 cycles of reuse after an activation step at 200 ºC for 3 h, between two consecutive runs. The products was confirmed by NMR, CHN and Mass analysis (^{1}H NMR (CD_3OD): δ 2.51 (s, 6H); δ 8.38 (s, 2H), Found: C, 66.79; H, 7.52; N, 25.95%, Calculated for $C_6H_8N_2$: C, 66.74; H, 7.46; N, 25.90%, MS: m/z 108 [M^+], b.p.: 152-154 ºC)

3.2 Mechanism

Scheme 1

Scheme 1 shows a probable reaction mechanism. As the cyclization requires light, O_2 and TiO_2, it can be deduced that the processes involved oxidation only. In presence of light and zeolite/TiO_2, diaminopropane and dihydroxypropane are cyclized to dihydo-2,5-DMP with loss of water molecules. The dihydro compound subsequently gets oxidized to 2,5-DMP via the formation of cation radical by the reaction with positive holes produced by the excitation of TiO_2. The other by-products are 5-methylpyrazine-2-methanol and 5-methylpyrazine-2-carbox-aldehyde.



Scheme 1

4. CONCLUSIONS

We have succeeded in the photochemical synthesis of 2,5-DMP through the intermolecular cyclization of diaminopropane and dihydroxypropane with the yield of 32.4 mol %. This is the first report, to our knowledge, on the synthesis of 2,5-DMP by photocatalysis. Our new route is environmentally friendly and is better than the conventional synthesis (i.e., starting from 1-amino-2-propanol), which gives mixture of products with low yields and requires high temperatures and tedious separation procedures.

REFERENCES

Chang, C. D. and Perkins, P. D., Process for making alkyl pyrazines, *US Patent*, 4,855,431(1989).

Fox, M. A.,Organic heterogeneous photocatalysis: Chemical conversions sensitized by irradiated semiconductors, *Acc. Chem. Res.*, 16(9), 314-321(1983). doi:10.1021/ar00093a001

Su, W. Y. and Knifton, J. F., Process for preparing pyrazines from hydroxylamines, *US Patent*, 4,788,289(1988).

Subba Rao, K. V. Srinivas, B. Prasad A. R. and Subramanyam, M., A novel one step photocatalytic synthesis of dihydropyrazine from ethylenediamine and propylene glycol, *Chem. Comm.*,(16),1533-1534(2000). doi: 10.1039/B003934I

Subba Rao, K.V. and Subramanyam, M., A novel one step photocatalytic synthesis of 2-methyl qunioxaline from o-phenylenediamine and propylene glycol over TiO_2/zeolite mediated system, *Chem. Lett.*,31(3), 234-235(2002). doi:10.1246/cl.2002.234

Subba Rao, K. V. Kandavelu, V. Srinivas, B. Subramanyam, M. and RavindranathanThampi, K., A novel route for the synthesis of pyrazine from N-(2,3-dihydroxypropyl) ethylenediamine over nanocomposite catalysts, *Chem. Comm.*,(21) 2706-2707(2003). doi:10.1039/B308520A

Wang, H. Partch, R. E. and Li, Y., Synthesis of alkyl benzimidazoles via TiO_2 mediated photocatalysis, *J. Org. Chem.*, 62(15) 5222-5225(1997). doi:10.1021/jo970253j